1.0

4.5
5.0
5.5

2.8

2.5

3.2

2.2

3.6

1.1

4.0

2.0

1.8

1.25

1.4

1.6

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

LEVEL II

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LASER RODS FABRICATED FROM <u>AMMRC</u> GROWN Nd:YAG

JUN 1978

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Jun 78   13p.

INTRODUCTION

The laser will be used extensively on the modern battlefield
to greatly improve the accuracy of new Army weapon systems. Some exam-
ples of applications are laser range finders in the XM-1 tank and other
armored vehicles and laser target designators for infrared guided mis-
siles and projectiles such as HELLFIRE and COPPERHEAD. While lasing
ability is found in gases, liquids, and solids (both crystalline and
noncrystalline), the laser preferred in the above Army application, be-
cause of its high efficiency and narrow spectral linewidth, is a single
crystal of a compound of yttrium oxide and aluminum oxide with small
additions of neodymium oxide as the active element. The compound
$Y_3Al_5O_{12}$ has a garnet crystal structure similar to the naturally occur-
ring gemstone $Mg_3Al_2Si_3O_{12}$, hence the name yttrium aluminum garnet, ac-
ronym YAG or Nd:YAG when doped with neodymium. Currently Nd:YAG laser
rods 6.4 mm diameter by 75 mm in length cost the Army more than $600
each. The objective of this program was to lower the cost of these
rods by employing a different growth technique, the heat exchanger
method (HEM)(1) shown schematically in Figure 1. This method was orig-
inally developed for the growth of large sapphire single crystals for
transparent armor applications (2) and has several cost saving features
when compared to the state-of-the-art Czochralski (CZ) technique (3).
Single crystal boules 3.0 to 3.7 cm diameter by 18 cm in length can be
routinely obtained by the CZ technique. A cross section of a boule of
this material is seen on the right in Figure 2 and Nd:YAG grown at
AMMRC by the HEM technique is seen on the left. In addition to the
size difference between the two crystals, another obvious difference is
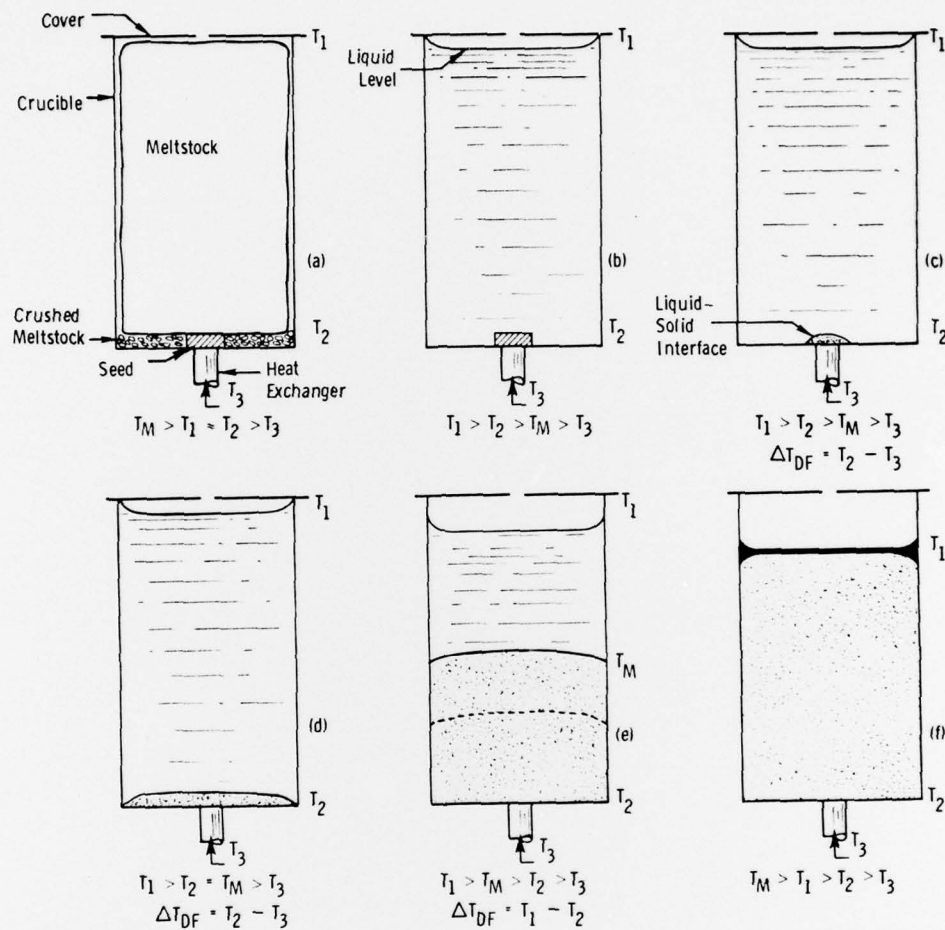the occurrence of facets, i.e., the flat faces of low index planes, on

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Cover

Crucible

Meltstock

Liquid Level

T_1

Crushed Meltstock

Seed

Heat Exchanger

T_2

T_3

(a)

$T_M > T_1 = T_2 > T_3$

(b)

$T_1 > T_2 > T_M > T_3$

Liquid-Solid Interface

(c)

$T_1 > T_2 > T_M > T_3$

$\Delta T_{DF} = T_2 - T_3$

(d)

$T_1 > T_2 = T_M > T_3$

$\Delta T_{DF} = T_2 - T_3$

T_M

(e)

$T_1 > T_M > T_2 > T_3$

$\Delta T_{DF} = T_1 - T_2$

(f)

$T_M > T_1 > T_2 > T_3$

(a) Crucible, cover, meltstock, and seed prior to melting.
   T_M = melting point of Nd:YAG
   T_1, T_2, T_3 = temperatures at various points in crucible.
(b) Meltstock melted.
(c) Seed partially melted to insure good nucleation.
   ΔT_{DF} = the temperature difference which is the driving force for crystal growth.
(d) Growth of crystal commences and covers crucible bottom.
(e) Unidirectional crystal growth. Note nearly planar liquid-solid interface.
(f) Crystal growth completed.

Figure 1.   Growth of Nd:YAG by the heat exchanger method (HEM).

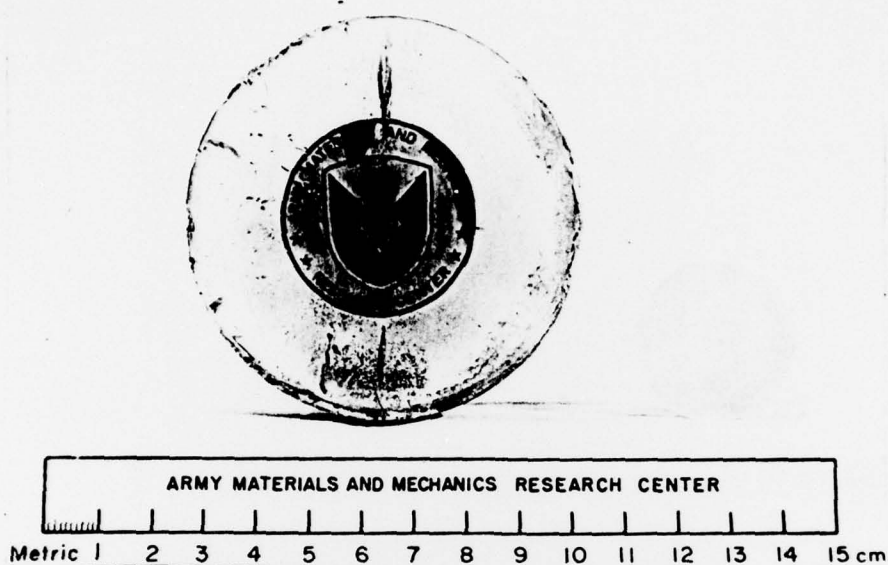78 06 12 063

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Figure 2.   Cross sections of Nd:YAG single crystals grown
by HEM (left) and Czochralski technique (right).

the CZ material. Faceting usually occurs during the growth of garnets,
and is very difficult to prevent when Nd:YAG is grown by the CZ tech-
nique (4). Aside from the flat faces of the crystal, the faceting also
manifests itself as a central strained core of material immediately
surrounding the axis of the boule. This limits the amount of the boule
that can actually be used for laser rods to no more than 26% of a 3-cm
diameter boule and 36% of a 3.7-cm diameter boule when 6.4-mm diameter
laser rods are considered. The efficiency of material utilization in-
creases with increasing boule diameter, and would increase more if the
material in the center of the boule could be used. For example, if
6.4-mm rods could be cut from a 7.5-cm diameter boule, including the
center, material utilization efficiency would increase to 83%.

The CZ growth technique for Nd:YAG is also inefficient from the
point of material utilization in that only about 50% of the melt can be
solidified in a controlled manner to produce a single crystal. The rest
of the melt is frozen quickly in the crucible and remelted later after
its stoichiometry is adjusted, or discarded when impurity levels become
too high. All the material grown by the HEM technique is solidified in
a controlled manner and 80% to 90% is available for laser rod fabrication.

Expensive iridium crucibles (>$10,000 each) are used in the CZ
growth of Nd:YAG while low-cost molybdenum crucibles ($200) are used in

HEM growth of Nd:YAG. Even though the iridium crucibles are reusable and the molybdenum crucibles are not, the latter are still less expensive. Also, since large crystals can be grown only from large crucibles, scale-up of the CZ technique is limited by the cost and availability of large iridium crucibles.

This paper will describe the transfer of the technology gained during the sapphire growth program for transparent armor to the growth of large Nd:YAG single crystals. It will describe starting materials preparation, modifications to the crystal growth process, and growth of 7.5-cm-diameter single crystals 9.7 cm high weighing 2000 g (the largest man-made Nd:YAG crystals in the world), fabrication of 3-mm-diameter by 30-mm-long laser rods, and the lasing ability of these test rods.

EXPERIMENTAL

Starting Materials

Starting materials did not present a problem during the sapphire growth program because of the availability of high purity sapphire crackle, i.e., cracked Vernueil grown boules with impurity levels of less than 40 ppm. These could be placed into crucibles with packing efficiencies of 70%. Any higher packing efficiency was unnecessary because more material in the crucible would "boil over" due to the 22% volume change of sapphire upon melting. No comparable Nd:YAG crackle was available, so meltstock had to be made in-house by sintering isostatically pressed cylindrical billets of mixed oxide powders to 65% to 75% of theoretical density. After firing, the billets would be small enough to slip inside the crucibles. Also, unlike sapphire, very accurate control of composition is necessary so that the melt stock is of the correct stoichiometry, $Nd_{0.03}Y_{2.97}Al_5O_{12}$. Incongruent vaporization of a constituent during sintering had to be minimized to maintain proper stoichiometry. To determine the process parameters for the Nd:YAG meltstock, a matrix experiment was conducted.

Starting materials were high purity oxides, 99.992% pure alumina,* 99.999% pure yttria,† and 99.0% pure neodymia.‡ These were weighed in correct proportions in 300-g batches to form Nd:YAG, i.e., 37.1 mol % Y_2O_3/62.5 mol % Al_2O_3/0.4 mol % Nd_2O_3. The powders were either mixed by allowing ethanol to boil away in a 2-gallon mill made

of high alumina, or milled in the same mill under several different conditions. The time of milling, the number of 1/2"-high alumina balls, and the milling fluid, ethanol or tertiary butanol, were systematically varied. After drying, the powders were placed in a rubber bag and iso-statically pressed at 30,000 psi to form rods 15 mm in diameter by 100 mm long. These were cut into 15-mm lengths with a dry diamond saw, and their bulk densities were taken by weighing and then measuring with a micrometer. Volumes were calculated from the physical dimensions. The rods were heated at 1650 C in air in a zirconia felt-lined $MoSi_2$ furnace for 1, 3, 10, or 10-1/4 hours. After firing determinations of weight loss, shrinkage, and bulk density were made. Phases present were determined by X-ray powder diffraction from powdered samples. The morphology of selected powders before and after milling were studied using a scanning electron microscope (SEM).

Crystal Growth

A hollow, helium-cooled tungsten/molybdenum heat exchanger was used for growth of sapphire to protect the seed and to extract heat from the crucible. With the furnace temperature held constant, the helium flow was increased and crystal growth commenced. This mode of growth resulted in a highly curved solid-liquid interface which was ade-quate for sapphire but would produce faceting in Nd:YAG (4). This mode of growth also produced large temperature gradients within the crystal and it was feared a serious cracking problem would result. Lastly, these hollow heat exchangers were not very durable and had to be re-placed after five or ten crystal growth runs. For these reasons the mode of crystal growth was changed to a "gradient freeze" mode where a temperature gradient was imposed on the melt by redesign of the heating element, and the furnace temperature varied with time according to a predetermined program.

A solid heat exchanger consisting of a tungsten cap, a graph-ite body, and a water-cooled copper base was substituted for the hollow helium-cooled heat exchanger. Although this heat exchanger did not have the flexibility for varying the seed temperature during the run independently of furnace temperature, it was more durable and still would prevent the seed from melting.

The crystal growth furnace contains a cylindrical graphite heating element. The element is naturally hotter at the bottom than at the top; this is opposite the way it should be for this mode of crystal growth. An engineering redesign study was undertaken to overcome this situation. A series of graphite muffles and a new type of graphite element were machined to try to overcome this difficulty.

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An actual crystal growth run takes 12 to 14 days from the time the furnace cover is closed until it is opened again. The first day is used for heat up and melting; the next half day is seeding; the next 8 to 9 days are growth; and the remaining 2-1/2 to 4-1/2 days are cool down. Growth rates vary between 0.3 and 0.8 mm/h. Temperature gradients within the furnace vary between 1 to 10 C/cm.

Fabrication

Slabs of Nd:YAG were rough cut with a diamond saw from selected regions of single crystals. The slabs were then cut into rectangular prisms, and subsequently centerless ground into 3-mm-diameter by 30-mm-long rods. The ends of the rods were ground and polished flat to within a tenth of a wavelength and parallel to each other to within 10.0 seconds. The ends were free of pits, scratches, and sleeks. They were then coated with an anti-reflective coating of MgF_2 a quarter wavelength thick or $\sim$4700 Å.

Characterization

As-grown boules were studied visually in normal and polarized light for gross flaws such as cracks and voids. The regions containing second-phase inclusions were determined with a microscope in oblique illumination. When necessary, plates were cut from crystals and polished. From these plates the progress of the solid-liquid interface during the growth process could be determined and correlated with changes in furnace conditions, especially the thermal gradient imposed by the furnace. The polished plates were observed with a transmitted light microscope and details of second phase and other scattering centers determined.

The scattering centers in the laser rods were determined by examining them visually under a strong light. The flatness of the ends was determined using an optical flat and then counting the fringes from a photograph. Fluorescent lifetimes were measured and compared against calibration curves to determine the actual concentration of Nd in the rods. Long pulse lasing efficiency was determined using an AN/GVS-5 cavity with a 20-µf capacitor.

RESULTS AND DISCUSSIONS

Starting Materials

Pressed meltstock billets had to be fired at 1650 C for one hour or more to attain densities above 65% of the theoretical density of Nd:YAG (4.56 g/cm^3). Figure 3 shows the results of several mixing
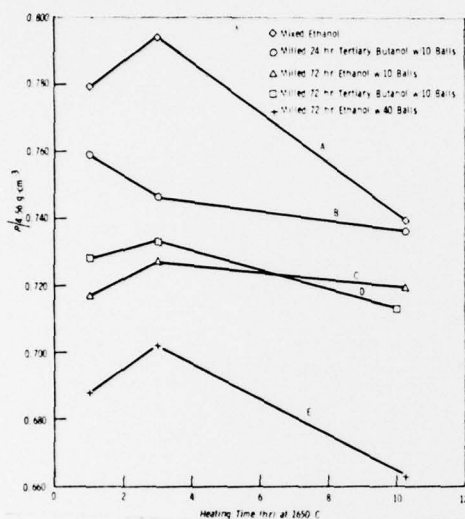
Figure 3. Densification of sintered billets of Nd:YAG expressed as bulk density of billets divided by the theoretical density of Nd:YAG as a function of heating time in air at 1650 C and different mixing and milling conditions.

and milling procedures on the density of sintered billets of Nd:YAG as a function of sintering time at 1650 C. In all cases a maximum is reached after three hours. This would be enough if the $Y_2O_3-Al_2O_3-Nd_2O_3$ system were a simple ternary. However, the $Y_2O_3-Al_2O_3$ binary contains two other compounds besides $Y_3Al_5O_{12}$: $YAlO_3$ ($\rho = 5.35$ g/cm^3) and $Y_4Al_2O_9$ ($\rho = 4.41$ g/cm^3) (5). When X-ray diffraction phase analysis was done on the pressed billets prepared under the conditions specified in Figure 3, it was found that they were usually not single-phase, but contained mixtures of all three of the above compounds plus traces of the starting materials. Figure 4 shows that heat treatment alone will not produce single-phase meltstock of only $Y_3Al_5O_{12}$. It is important to mill the material to insure good mixing and to break up agglomerates which would react together and form unwanted compounds. Previous studies (6) had indicated that the meltstock must be single-phase YAG to get a controlled melt and the desired stoichiometry in the Nd:YAG crystal.

Furnace Design

The furnace element used for the sapphire growth program, on the right in Figure 5, is a "ribbon" type where power is brought in from the top. The current follows on a ribbon or sinusoidal path through the element as evidenced by the pitted regions on its surface. This type of heating element contains alternate hot and cold spots along the ribbon which produce circumferential thermal gradients and is hotter at the bottom than at the top. This was not a problem for growth of sapphire because the cooling efficiency of the helium-cooled heat exchanger could compensate for the reversed gradient and the hot spots and still produce a sufficient thermal gradient for growth. With Nd:YAG where a flat solid-liquid interface is needed, the helium-cooled heat exchanger is too powerful. It was necessary to build the upward temperature gradient into the heating element. It was difficult to machine the desired taper in a heating element such as the one on the right of
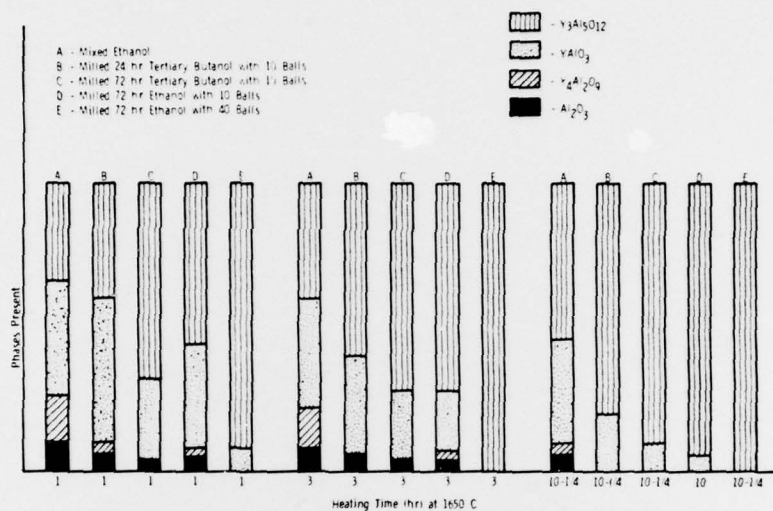
Figure 4. Phases present after heating powder mixtures of
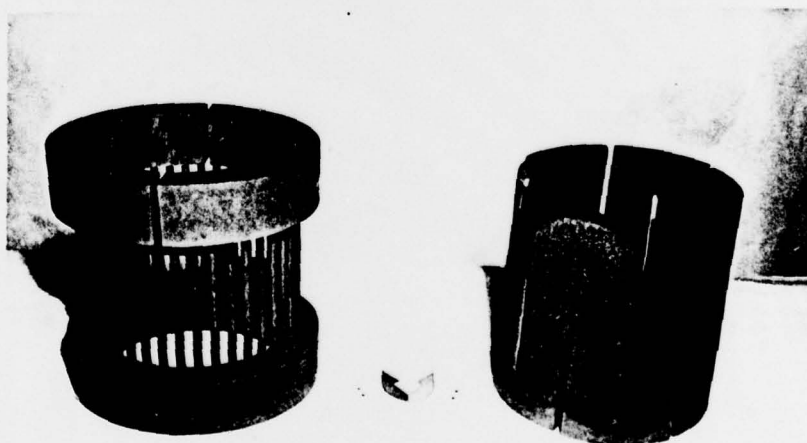composition 37.1 m/o Y_2O_3/62.5 m/o Al_2O_3/0.4 m/o Nd_2O_3.

Figure 5. Graphite heating elements used in HEM furnace: "Birdcage"
type is on the left and "ribbon" type is on the right. Note pitted
regions on "ribbon" type indicative of electric current path.

the figure. Interim solutions, such as contoured muffles which fit inside the element, were not totally satisfactory because not enough of a gradient would be introduced this way. Therefore, the furnace element design at the left was selected. This "birdcage" design is all graphite and consists of a complete bottom ring, a split upper ring, and many tapered rods connecting the upper and lower portions. The individual rods can be tapered as needed to introduce the desired temperature gradient. Initially, the power feeds came through the top ring. It was found that because the power feeds act as powerful heat sinks the gradient in the element was still not satisfactory. This problem was corrected by inverting the element, which brought the power feeds to the bottom of the element. With the heat sink at the bottom, a sufficient gradient, i.e., 10 C/cm was built into the element over the 12-cm height of the crucible.

Crystal Growth

Unfaceted Nd:YAG single crystals have been grown by HEM. Scale-up efforts over the last several years have increased crystal sizes from 5.32 cm diameter by 3.50 cm high weighing 355 g to 7.62 cm diameter by 10.5 cm high weighing 2180 g, as seen in Figure 6. It is believed that the 2180-g crystals are the largest ever made in the world. The crystals shown were doped at levels between 0.25 and 0.75 at. % Nd which is below the 1.1 at. % required. These crystals are free of scattering centers throughout 90% of their volume. At dopant levels of 1.1 at. %, crystals are free of scattering centers for no more than 50% of their
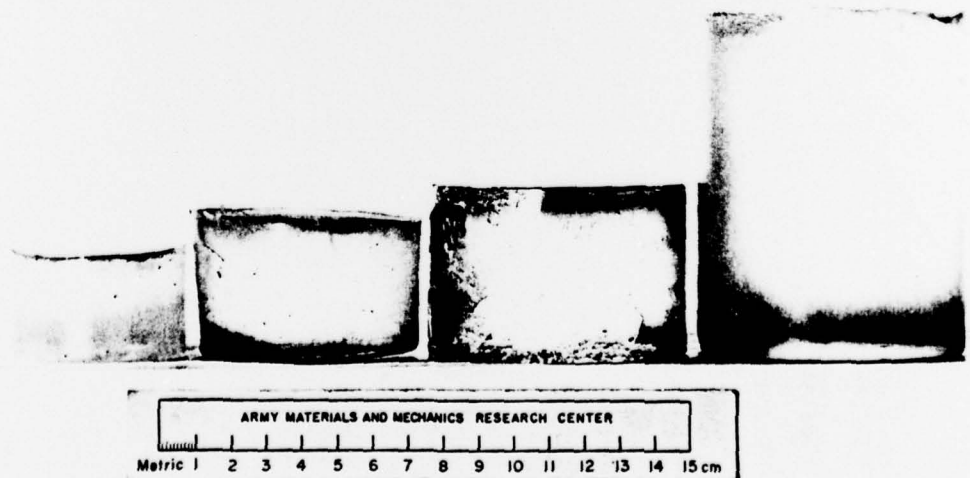

Figure 6. Scale-up of Nd:YAG single crystals.

volume. This is because growth becomes more difficult with greater dopant concentrations. More careful attention must be paid to attaining and maintaining stoichiometry because of the complex phase equilibria (5), and to achieving the required temperature gradients and growth rates. Nd:YAG must be grown slower than undoped YAG (7). While an average growth rate can be calculated from crystal size and time of growth, the instantaneous growth cannot yet be measured directly. Thus, although the change of growth rate with time should equal zero, it does not. This means that different parts of the crystal grow at different rates.

Scattering centers can be seen with the unaided eye. Detailed structure (Figure 7) can be seen with a transmitting light microscope. The scattering centers are channels which are mostly empty except for some second-phase α-Al_2O_3 or $YAlO_3$, depending upon whether the liquid is Al_2O_3-rich or Y_2O_3-rich. This structure is characteristic of one formed when the planar solid-liquid interface breaks down because of constitutional supercooling (8). The channels are originally liquid regions which freeze well below the melting point of the rest of the crystal because they contain higher concentrations of impurities and/or dopant. Thus the crystal freezes around them. When they finally freeze, the material contracts leaving mostly empty space in the channels.

Figure 7. Optical photomicrographs of second-phase inclusion in YAG single crystals. Plate a - inclusion of perovskite; plate b - inclusion of α-alumina. The arrows denote voids in channels containing inclusions. These voids were created due to the liquid-solid contraction. Therefore it could be concluded that the second-phase liquid solidified in already solid YAG matrix.

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Laser Rod Fabrication

Laser rods were fabricated from the lower half of a nominally 1.1 at. % Nd:YAG. As seen in Figure 8, these were 3 mm diameter by 30 mm long and were cut along a radius of the single crystal. The size was dictated by the lasing chamber which was used for characterization.

Figure 8. 3 x 30 mm laser rods made from AMMRC-grown
Nd:YAG single crystal - scale 1:2.

Lasing Properties

The fluorescent lifetime of the rods was determined to be 254 ± 2.5 µsec. When compared with predetermined calibration curves re-relating fluorescent lifetime to Nd concentration in the rods, AMMRC rods were found to have a concentration of 0.6 to 0.8 at. % Nd.* Lasing efficiency for long pulse operations is seen in Figure 9. The slope of the curve η = 0.2%. This is less than obtained from CZ Nd:YAG where
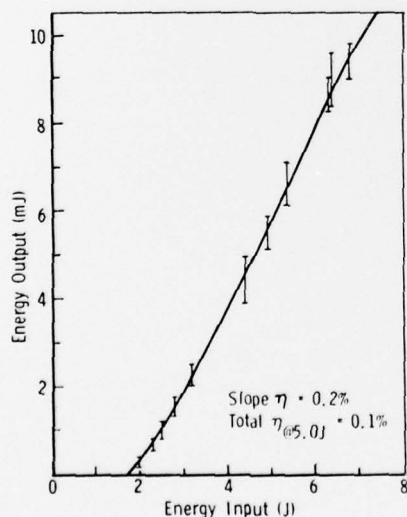

Figure 9. Energy output versus energy input for HEM-grown laser rods. R = 75%.

*STROZYK, J. ERADCOM, Private Communication, 28 February 1978.

$\eta \approx 1.0\%$. This value is also dependent upon Nd concentration. The purpose of these tests was to demonstrate that material made by HEM could lase, which it did. No attempt was made to optimize laser performance. It did appear, however, that performance could have been better if the material contained higher concentration of Nd. Studies are now underway to increase Nd concentration in AMMRC laser rods, including a detailed investigation of the ternary phase equilibrium diagram in the region near $Y_3Al_5O_{12}$.

SUMMARY

This paper has described HEM and its application to the growth of Nd:YAG. It has detailed the advantages of growing Nd:YAG by HEM as compared to the state-of-the-art CZ technique. The technology transfer from a technique originally developed for the growth of large sapphire ingots has been covered. The particular problem areas have been melt-stock preparation, furnace redesign to insure a planar solid-liquid growth interface and hence facet-free crystals, and definition of process parameters. HEM-grown Nd:YAG does lase, and studies are now underway to optimize its lasing properties by increasing Nd concentration in the laser rods.

ACKNOWLEDGMENTS

The authors wish to thank J. Smith, Crystal Optics, Inc., for laser rod fabrication, R. F. Belt, Litton Industries, Inc., for the anti-reflective coatings, J. Strozyk, ERADCOM, for measurement of lasing properties, and W. H. Earle, AMMRC, for valuable technical assistance throughout the program.

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